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A COMPARISON OF DEFLAGRATION RATES AT ELEVATED PRESSURES AND TEMPERATURES WITH THERMAL EXPLOSION RESULTS

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TITLE OF PAPER A COMPARISON OF DEFLAGRATION RATES AT ELEVATED PRESSURES AND TEMPERATURES WITH THERMAL EXPLOSION RESULTS

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Abstract. The deflagration rate of HMX-based explosives has previously been correlated with the violence of thermal explosion experiments. In particular, HMX-based materials that experience deconsolidative burning at elevated pressures (i.e. P = 200 – 600 MPa) also produce significantly more violent thermal explosions. We now report deflagration rates at elevated temperatures (i.e. T = 150 – 180C) and moderate pressures (i.e. P = 10 – 100 MPa). These conditions more closely mimic the pressures and temperatures of an explosive shortly after ignition of a thermal explosion. Here, we discuss the deflagration rates of HMX-based explosives at elevated temperatures and their usefulness to predict the thermal explosion violence of the same materials.

Keywords: Thermal explosion, deflagration rates, HMX.
PACS: 82.33.Vx, 82.30.Lp, 82.40.Fp.

INTRO

The deflagration behavior of an explosive is an important element of the multistage thermal explosion process and has been correlated with the degree of explosive violence. A material that burns or deflagrates rapidly will generate pressure rapidly leading to a more violent rupture of the confining vessel. The burn rate of a material is dependent on multiple variables including the intrinsic rate of molecular decomposition at elevated temperature, thermal transport rates, how readily the material is damaged, and how much surface area is created.

Previous studies have correlated the burn rates of HMX-based formulations with the violence of scaled thermal explosion tests (STEX). In the burn rate studies, the HMX-formulations LX-04, LX-10, and PBX-9501 were found to all burn with similar rates between 10 and 150 MPa [1]. Above 150 MPa, LX-10 and PBX-9501 burned rapidly and erratically. The presumed mechanism is burning-induced deconsolidation, resulting from the evolution of damage and fractures in the explosives. Fractures increase the available surface area for burning and enable transport of hot product gases beyond the conductive front, resulting in a transition to the more violent mode of convective burning [1]. STEX results demonstrated a significant increase in violence of the LX-10 and PBX-9501 relative to LX-04 [2]. Hence, the violence of the thermal explosion was correlated with the observation of erratic and presumably deconsolidative burning.

This is an interesting observation, but has limited value, since it provides little opportunity to rank the violence of different materials based on their burn rates. In an attempt to provide more quantitative predictions of explosion violence, we have measured the burn rates of explosives at elevated temperatures and pressures. Previous burn rate measurements were only made at ambient temperature. In a true cookoff scenario the material will experience a significant time at elevated temperature, hence the burns reported here more

closely approach conditions of interest. This paper compares the burn rates of multiple HMX-based explosives at elevated temperatures and discusses the thermal explosion violence in the context of these burn rate measurements.

EXPERIMENTAL PROCEDURE

Materials

The formulation details for all the materials are listed in Table 1; all the samples were pressed to ca. 98% theoretical maximum density. The PBXN-9 formulation listed in Table 1 is based on the certificate of analysis for this specific lot.

Table 1. Formulation details

Material	Formulation (wt %)
LX-04	85% HMX, 15% Viton A
LX-10	95% HMX, 5% Viton A
PBX-9501	95% HMX, 2.5% Estane, 2.5% BDNPA/F
PBXN-9	92.8% HMX, 5.3% Dioctyl Adipate (DOA), 1.9% Hytemp 4454

Burn rates are measured using the LLNL high pressure strand burner. This experimental technique has been described in detail [1, 3]. Briefly, burns are performed under constant volume in an atmosphere of argon. The vessel pressure is measured *in situ* throughout the burn, and burn progress is monitored via multiple silver break wires spaced throughout the sample. A typical sample consists of nine individual pellets (0.25 in diameter by 0.25 in tall) and 10 burn wires, the exterior surface is encapsulated by an organic-polymeric material to prevent flame spread down the sides. In a typical burn, the sample is pre-pressurized, initiated via an igniter train and the resulting burn causes a rise in vessel pressure on the order of 3-5 times the initial pressure. Many towers are burned to investigate a pressure range of 10-600 MPa. Samples are pre-heated *in situ* (1.5 ºC/min, 2+ hr hold) and burned at elevated temp.

Scaled thermal explosion (STEX) experiments were designed and performed at LLNL. A detailed description of the STEX experiment is provided in the literature [2]. Briefly, the experiment involves packing a 410 cc cylindrical vessel (2 in diameter by 8 in height) with explosives and heating the sample slowly (1ºC/hr) until it explodes. The heating configuration is designed to uniformly heat the cylindrical surfaces and achieve thermal ignition at the center. Violence is quantified by the wall or fragment velocity measurements (radar horns and/or photonic Doppler velocimetry [PDV]), strain gauges around the vessel, and post-experiment visual assessment of the vessel damage. Three wall velocities are listed, obtained from three separate locations on the STEX vessel on each experiment. The experiments discussed here were all designed to withstand pressures up to 200 MPa.

It is well-established that HMX undergoes a polymorph transition from β to δ, and that this transition is pressure- and temperature- dependent [4]. By confining the material during heating the transition can be suppressed, and HMX will begin to decompose directly from β-form. STEX experiments were designed to study both polymorphs. In some experiments, the vessel was fully filled and HMX began decomposition from the β-form. In other experiments, the vessel was under-filled, leaving 7% ullage for the HMX to fill as the material underwent the β→δ transformation.

RESULTS AND DISCUSSION

Previous work on LX-04 has shown that at ambient temperature the material burns laminarly over a wide pressure range (10 – 500 MPa). At 150 ºC the burn rates are nearly identical to the ambient temperature rates. At T > 167 ºC, however, LX-04 burns considerably faster. It was hypothesized that the acceleration in burn rate results from increased porosity introduced by the β-δ transition that HMX undergoes at ~ 159 °C [1]. The STEX results for LX-04 are listed in Table 2. Based on the wall velocity data, the strain rate data, and the recovered fragment numbers both the δ and β-phase exhibit relatively low violence.

One key difference between the strand burner experiments and the STEX experiments is the free volume available for HMX expansion in the strand burner vessel. The δ-phase crystal is ~7% larger (by volume) than β-phase. However, in an unconstrained environment a pressed part can expand at least 17% due to crystallographic mismatch of the HMX particles and binder interactions[5], resulting in significant porosity in the δ-phase pressed part. In the strand burner

experiments, the explosive is allowed unrestricted expansion and the parts are expected to have a high degree of porosity. In contrast, the δ-phase STEX experiments are only allowed ~7% ullage, hence there is enough space for the HMX to phase convert but there should be much less porosity.

Table 2. STEX results

Expt Num	Sample		Wall speed (m/s)	Frag-ments	Log Strain Rate (s^{-1})
10	LX-04	β	NA	1	NA
9	LX-04	δ	800, 640, 0	1	NA
29	LX-04	δ	1100, 0, 0	1	1.7
59	PBXN9	β	425, 150, 130	3	1.8
57	PBXN9	δ	710, 275, 690	3	2.7
54	LX-10	β	1100, 1500, 3000	300	3.2
11	PBX-9501	β	1700, 1600, 1900	many/ small	3.0
8	PBX-9501	δ	300, 800, 700	16	NA

Figure 1 displays the burn rate results for PBXN-9. The rates increase at 150 and 184°C temperatures presumably due to porosity induced by evaporation and/or decomposition of the plasticizer, DOA and/or the HMX-phase transition [6]. In spite of these accelerated burn rates, the STEX results indicate that explosions of PBXN-9 are less violent than explosions of LX-10 and PBX-9501. In the β-phase STEX experiments, the vessel is fully sealed and evaporation of the DOA is expected to be heavily suppressed. The PBXN-9 in the β-phase STEX experiments is therefore not expected to have the same degree of porosity as the PBXN-9 in 150 °C strand burner experiments. For that reason, it is not surprising that the β-phase STEX explosions are relatively less violent despite the rapid burn rate observed at 150 ºC.

According to the results in Table 2, the δ-phase explosions were slightly more violent than β-phase. It is possible that there are small cracks present in δ-phase PBXN-9, which allow for convective flame spread and a higher violence. However, it could be argued that the soft and malleable binder and/or plasticizer will fill many of these. In which case, this data could provide evidence that the HMX-polymorph plays a role in the violence. More work is necessary to explore this hypothesis.

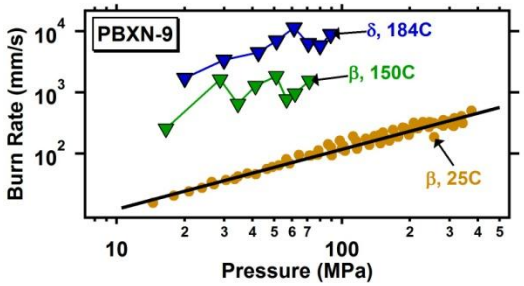

Figure 1. Burn rate measurements for PBXN-9

Strand burner results for LX-10 are shown in Figure 2. The burns at 25 and 150 ºC are similar; the burn rates at 180 ºC are faster, presumably due to increased porosity in the sample. Figure 3 shows the strand burner results for PBX-9501. There are two notable differences between the PBX-9501 results and the other materials discussed here. First, the rates measured at 173 °C are faster than the other formulations. At this temperature the energetic plasticizer, BDNPA/F, is expected to have evaporated. However, there may be some residue in the strand that accelerates the burn above the rate seen in PBXN-9 and LX-10. The second difference is in the 150 ºC burns. Here one can see that material begins to burn like pristine material, but suddenly accelerates. This behavior is similar to the behavior of burns at elevated pressure where deconsolidation was hypothesized.

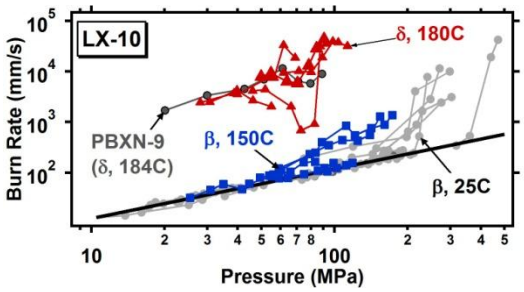

Figure 2. Burn rate measurements for LX-10

The STEX test for β-phase LX-10 produced a fairly violent explosion; no data are available for δ-phase. Thermal explosion tests by Atwood et al. indicate that δ-phase LX-10 is more violent than β-phase [7]. The STEX results for β-phase PBX-9501 also show a significant increase in violence

relative to LX-04 and PBXN-9. In fact, the vessel fragments were too numerous and small to count, indicative of an extremely violent thermal explosion. Interestingly, these results indicate that the β-phase is more violent than δ-phase. In fact, the δ-phase results appear to have wall velocities that are similar to the δ-phase results for LX-04 and PBXN-9.

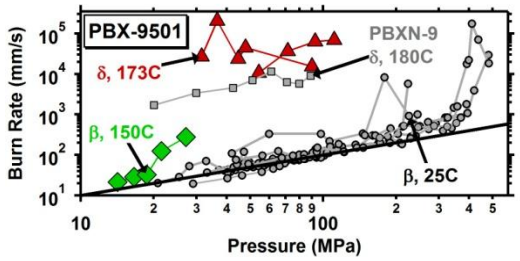

Figure 3. Burn rate measurements for PBX-9501

CONCLUSIONS

Previous work established a correlation between materials that deconsolidatively burn at elevated pressures and ambient temperature, and materials that produce more violent thermal explosions [1, 2]. Specifically PBX-9501 and LX-10 experienced elevated-pressure deconsolative burning and were considerably more violent than LX-04. The new PBXN-9 data presented in this paper are consistent with this correlation.

We hypothesized that elevated-temperature burn rates would allow for more rigorous predictions of thermal explosion violence. Based on the results presented here, however, it appears that the elevated temperature burn rate experiments and the STEX experiments are sufficiently different to make correlations difficult. In particular, the porosities of HMX-based explosives are expected to be significantly greater in the strand burner experiments than in the STEX experiments. The strand burner results may provide more insight if interpreted in the context of lightly confined or unconfined experiments. For example, thermal explosion results by Tringe et al. [8, 9], in which lighter confinement was used, suggest that PBX-9501 has a higher propensity to burn relative to LX-10, especially after the vessel ruptured. This observation is consistent with the faster burning rates of PBX-9501 at 180 ºC and the unusual burn behavior at 150 °C.

A particularly interesting outcome of this study is the relative violence of β vs. δ phase HMX. It appears that the elevated violence observed in β-phase thermal explosions is correlated with deconsolidative burning at ambient temperature (e.g., PBX-9501 and LX-10). In materials that do not deconsolidatively burn at ambient temperature (i.e. PBXN-9), the δ-phase is more violent than the β-phase although neither phase is extremely violent.

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REFERENCES

1. Maienschein, J. L., et al., "Deflagration of HMX-Based Explosives at High Temperatures and Pressures", *Prop, Exp, & Pyro*, **29**, 287, (2004).
2. Wardell, J. F. and Maienschein, J. L., "The Scaled Thermal Explosion Experiment", *12th Int. Det. Symp.*, 384, (2002).
3. Glascoe, E. A., et al., "PBXN-9 Ignition Kinetics and Deflagration Rates", *JANNAF 24th PSHS*, **1**, 1, (2008).
4. Landers, A. G. and Brill, T. B., "Pressure-Temperature Dependence of the beta-delta Polymorph Interconversion In Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine", *J. Phys. Chem.*, **84**, 3573, (1980).
5. Weese, R. K. and Burnham, A. K., "Coefficient of Thermal Expansion of the β and δ Polymorphs of HMX", *Prop, Exp, & Pyro*, **30**, 344, (2005).
6. Glascoe, E. A., et al., "The Influence of the Binder, Plasticizer, and Degree of Porosity on the Burn Rate and Behavior of the HMX-based Explosive PBXN-9", *in preparation*, (2011).
7. Atwood, A. I., et al., "Energetic Material Response in a Cookoff Model Validation Experiment", *12th Int. Det. Symp.*, 112-117, (2002).
8. Tringe, J. W., et al., "Time-Sequenced X-Ray Observation of a Thermal Explosion", *APS - SCCM*, **1195**, 424-427, (2009).
9. Tringe, J. W., et al., "The role of binder in deflagrating HMX-based explosives", *in preparation*, (2011)